

JOURNAL OF  
THE  
INDIAN INSTITUTE OF SCIENCE

VOLUME 44

APRIL 1962

NUMBER 2

REACTION BETWEEN DISULPHUR MONOXIDE AND  
PIPERIDINE IN ORGANIC SOLVENTS

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Received on February 1, 1962

ABSTRACT

When the products of combustion of sulphur in oxygen at low pressure are passed through cooled organic solvents, fairly pure solutions of disulphur monoxide can be obtained in the case of carbon tetrachloride. Toluene and anisole solutions contain considerably large quantities of sulphur dioxide associated with disulphur monoxide. In the presence of piperidine, the solvent effect is nearly same in all the three cases on account of the reactivity of piperidine with the oxides of sulphur. The influence of piperidine is observed in the variation of the products of hydrolysis in alkali and acid media. The nature of the sulphur compounds with piperidine has also been investigated with anhydrous hydrogen iodide.

INTRODUCTION

There has been a considerable controversy over the nature of the products of combustion when sulphur is burnt in oxygen at low pressures.<sup>1-8</sup> The exact nature of the products present in the gaseous state may perhaps be realised more correctly if the products are fixed up by allowing them to react with a reactive substance like an alkali present in the inert organic solvent employed for absorption. Obviously an alkali hydroxide cannot be employed for absorption as it is not soluble in an inert solvent like carbon tetrachloride or toluene. Hence organic bases which are soluble in organic solvents have to be thought of for fixing the products of combustion *in situ*. In the present investigation the organic base chosen is piperidine which is stronger than ammonia and pyridine. ( $K_B$ : for piperidine  $1.6 \times 10^{-3}$ , ammonia  $1.8 \times 10^{-5}$  and pyridine  $2.3 \times 10^{-9}$ ).<sup>9</sup> Carbon tetrachloride (F.P.  $-22^\circ\text{C}$ ), anisole (F.P.  $-37.3^\circ\text{C}$ ) and Toluene (M.P.  $-95^\circ\text{C}$ ) were used as solvents for dissolving the products of combustion.

## EXPERIMENTAL

(1) *Combustion of Sulphur*: The quartz apparatus described earlier<sup>4</sup> was used for the combustion of sulphur in oxygen at low pressure (7–15 mm. of Hg.). For carbon tetrachloride and anisole a temperature of  $-15^{\circ}\text{C}$  was maintained while toluene was maintained at  $-76^{\circ}\text{C}$  with the help of carbon dioxide snow and alcohol.

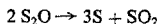
The solubility of sulphur dioxide in carbon tetrachloride at  $-15^{\circ}\text{C}$  is negligible and therefore all the sulphur dioxide could be pumped off easily from the solution. But in the case of anisole and toluene, the solvents retained considerable quantities even after pumping. The disulphur oxide solutions obtained in such solvents were always associated with considerable amounts of sulphur dioxide.

The total sulphur and sulphur dioxide contents of such solutions were determined making use of mercury decomposition method of the lower oxide as described earlier.<sup>7</sup> The analytical results of the decomposition experiments are given in Table I.

TABLE I  
Mercury decomposition of Disulphur Oxide in Organic Solvents  
(Concentration of sulphur and its compounds are expressed in  
g. atom of S  $\times 10^6$  per g. of solvent)

Solvent	SO <sub>2</sub>	Elemental Sulphur	Total S	S <sub>2</sub> O	% S <sub>2</sub> O
Carbon tetrachloride	0.601	1.783	2.384	2.384	100.00
Toluene	7.57	2.14	9.71	2.84	29.35
Anisole	17.60	12.70	30.30	16.93	55.87

It is perhaps necessary to give the following explanation to understand the significance of the analytical results indicated above. The organic solvent may be expected to contain disulphur monoxide, sulphur dioxide and elemental sulphur dissolved in it produced by the decomposition of the lower oxide according to the equation:



When the solution samples are shaken with mercury, mercury sulphide is produced and the corresponding amount of sulphur dioxide is liberated:



Experiments with carbon tetrachloride solutions indicated that the ratio of sulphur dioxide to elemental sulphur was about 1 : 3. It was thus possible to

obtain disulphur monoxide solutions in carbon tetrachloride practically free from sulphur dioxide and elemental sulphur although such 'pure' solutions of disulphur oxide were not always possible to get as considerable amount of elemental sulphur was associated with it, produced during the dissolution of the lower oxide in the organic solvent.

Such straight forward calculations could not be made with solutions of anisole and toluene. The elemental sulphur was found to be too small when compared with their sulphur dioxide content. An estimate of the lower oxide content could be made by assuming that all the elemental sulphur present was produced during the mercury decomposition of the disulphur monoxide.

Disulphur monoxide is known to<sup>6,7</sup> give rise to sulphide, sulphite, thiosulphate and elemental sulphur on treatment with alkali. These analytical results have been explained on the basis of three reactions which the lower oxide undergoes during hydrolysis: (1) Hydrolysis (H), (2) Thionisation and Decomposition (D). By estimating the products of hydrolysis it was possible to compute the amount of disulphur oxide present in the organic solvent. The results obtained for hydrolysis, thionisation and decomposition of toluene solutions were comparable with those of carbon tetrachloride. It has to be pointed out, however, that the amount of sulphur dioxide retained in toluene will be very much higher than in carbon tetrachloride owing to the high solubility of the gas in the solvent at low temperature. Anisole solution of the lower oxide of sulphur is of special interest on account of its higher content of the oxides of sulphur. Anisole being an ether, forms complexes both with sulphur dioxide and disulphur monoxide by the coordination of the electrons from the oxygen with the sulphur atom. The results of acid hydrolysis were also of similar type except that no sulphide was formed.

(2) *Reaction between disulphur monoxide and piperidine in organic solvents:* Piperidine solutions (2g. in 30-40 ml. of the organic solvent) were employed to absorb the gaseous products obtained during the combustion of sulphur in oxygen at low pressures. The solutions obtained by absorbing the products of combustion were hardly pale yellow in contrast to the deep yellow or orange solutions obtained in the absence of piperidine in these solvents. Aliquots of these solutions were used to study the hydrolysis in both alkali and acid media and also to study the reaction with hydrogen iodide.

(a) *Alkali Hydrolysis:* An aliquot of the solution of disulphur monoxide in the organic solvent was shaken with 25 ml. of sodium hydroxide containing a little of cadmium hydroxide suspension. No sulphide was detected in the case of carbon tetrachloride and anisole solutions; there was a little amount of cadmium sulphide with toluene solution which was separated and estimated. There was no elemental sulphur produced during alkali hydrolysis. The filtrate was analysed for sulphite and thiosulphate. It is interesting to note that among the products of alkali hydrolysis thiopiperidines were also present.

A small part of this remained in suspension in aqueous layer and a part of it remained in solution of the organic layer. The solid could be identified as thiopiperidine by the characteristic smell and melting point  $72^{\circ}\text{C}$ . Attempts to isolate the individual thiopiperidines by paper chromatographic method were not successful. Oxidation with chloramine-T indicated that the solid contained mostly monothiopiperidine (96%) with a little of dithiopiperidine (4%). Such an estimation could not be made in the case of anisole solution as the solvent itself undergoes oxidation by the reagent. The thiopiperidine content in anisole was taken as the difference between the total sulphur content as determined by acid hydrolysis and alkali hydrolysis. The analytical results of hydrolysis reactions are given in Table II.

(b) *Acid Hydrolysis*: The previous experimental technique was used to study the acid hydrolysis employing dilute acetic acid (2N). The organic layer was separated and was found to contain neither elemental sulphur nor thiopiperidines. The aqueous acidic solution was made up to a volume and was analysed for sulphite, thiosulphate, trithionate and tetrathionate.<sup>11,12</sup> There was no elemental sulphur in the aqueous phase also. The analytical results of the acid hydrolysis are also included in Table II.

TABLE II  
Results of Hydrolysis Experiments  
(Concentration of sulphur compounds are expressed in g. atom of  
 $\text{S} \times 10^6$  per g. of the solution)

	Alkali Hydrolysis			Acid Hydrolysis		
	Carbon tetra- chloride	Toluene	Anisole	Carbon tetra- chloride	Toluene	Anisole
1. Sulphide	.....	.....	1.85	.....	.....	.....
2. Sulphite	.....	11.22	24.02	23.43	18.79	22.05
3. Thiosulphate	.....	5.93	15.52	22.96	5.10	13.65
4. Thiopiperidine	.....	10.12	3.5	10.12	.....	.....
5. Trithionate	.....	.....	.....	.....	1.92	8.63
6. Tetrathionate	.....	.....	.....	.....	3.82	0.99
7. Total Sulphur	.....	27.27	44.99	56.51	29.63	45.32
					57.20	

It can be made out from the analytical results that the total amount of sulphur formed by alkali hydrolysis agrees reasonably with the total quantity obtained by acid hydrolysis. The significance of these analytical results and the possible mechanisms for hydrolytic reactions are discussed later.

(c) *Reactions with hydrogen iodide*:—It has been shown that sulphur in reactive sulphur compounds is reduced by anhydrous hydrogen iodide to liberate hydrogen sulphide and a corresponding amount of iodine is set free. Oxygen in association with sulphur is converted into water and an equivalent amount of iodine is produced. By estimating hydrogen sulphide and iodine it is possible to get an idea of the nature of sulphur compound.<sup>7</sup>

The hydrogen iodide reactions could not be carried out with anisole solutions as the solvent itself would react with the reagent to form phenol and methyl iodide<sup>13</sup>. Hydrogen iodide reactions were carried out with carbon tetrachloride and toluene solutions. The ratio of iodine to hydrogen sulphide formed was calculated in each case. From analytical results of hydrolysis reaction also it was found that all the sulphur present in the organic solvent was reduced by hydrogen iodide. The significance of the analytical results presented in Table III is discussed in a later section.

TABLE III  
Reaction with Hydrogen Iodide  
(Concentration expressed in g. atom of S  $\times 10^2$  per g. of solution)

Solvent	Alkali hydrolysis					
	H <sub>2</sub> S	I	I/H <sub>2</sub> S	Sulphite	Thio-sulphate	Total Sulphur
Carbon tetrachloride .....	5.02	28.87	5.75	3.55	1.26	4.81
Toluene .....	4.27	27.04	6.33	3.46	0.92	4.38

#### DISCUSSION

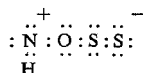
Results presented in Table II indicate that no sulphide is produced in the alkali hydrolysis of carbon tetrachloride and anisole solutions of sulphur oxides. If disulphur monoxide were in 'free' condition, a considerable portion would have undergone hydrolysis giving rise to sulphide. It may therefore be inferred that disulphur monoxide has formed a compound with piperidine. This is also supported by the fact that in presence of piperidine the usual orange, red or deep yellow colour of the disulphur monoxide solution is not noticed.

The sulphite produced in the alkali reaction is partly due to the sulphur dioxide obtained during the combustion of sulphur and partly due to the

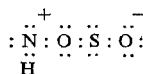
decomposition of disulphur monoxide. Sulphur dioxide is known to form complexes with piperidine<sup>14</sup> and is observed to behave like a sulphite in aqueous solution towards thiopiperidines<sup>15</sup> as well as chloramine - T.<sup>10</sup>

From physicochemical measurements it has been shown recently that the molecular structure of disulphur monoxide is similar to sulphur dioxide with the following parameter for S<sub>2</sub>O,<sup>16</sup> S - S distance 1.884 Å, S - O distance 1.465 Å, S - S - O angle 118°5'. The corresponding parameters for SO<sub>2</sub> are: S - O 1.432 Å and O - S - O angle 119°33'. The disulphur monoxide also has a bent structure similar to sulphur dioxide but with the oxygen atom of the latter being replaced by sulphur. The S - O bond in disulphur monoxide also has considerable amount of double bond character comparable to that of sulphur dioxide.<sup>17</sup> One may therefore expect that disulphur monoxide forms a complex with piperidine similar to sulphur dioxide.

The lone pair of electrons on the nitrogen atom of piperidine may coordinate with the sulphur atom in disulphur monoxide giving rise to the compound

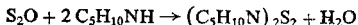


similar to the one with sulphur dioxide:

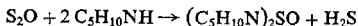


If this complex *formed*, was only an adduct, it would have given rise to sulphide on hydrolysis; however, the analytical results show that no sulphide is formed. It may therefore be inferred that disulphur monoxide has reacted differently towards piperidine. The probable products of reaction between disulphur monoxide and piperidine may be the following:

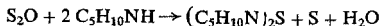
- (1) Formation of a dithiopiperidine with the elimination of water:



- (2) Formation of thionyl piperidine with the liberation of hydrogen sulphide:



- (3) Formation of monothio piperidine along with elemental sulphur and water:

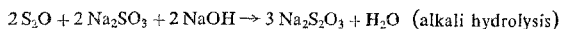


All the three compounds that may be expected from the above three types of reactions have been found among the products of reaction. The nature of these different species has been investigated in detail and reported elsewhere.<sup>18</sup>

If thionyl piperidine and hydrogen sulphide are formed, the hydrogen sulphide may react with piperidine. Hydrogen sulphide is reported to form a complex with piperidine at low temperatures only ( $-70^{\circ}\text{C}$ ) and is non-existent above  $-5^{\circ}\text{C}$ , as it loses hydrogen sulphide continuously.<sup>19</sup> Only in the case of toluene solutions containing piperidine a small amount of sulphide is produced in alkali hydrolysis.

It is also probable that monothio piperidine is formed and the elemental sulphur dissolves in piperidine to form other thiopiperidines.

The formation of thiosulphate in alkali and acid hydrolysis reactions of disulphur monoxide solutions in carbon tetrachloride is explained on the basis of thionisation :

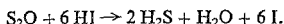


There is no formation of polythionates in alkali hydrolysis. Solutions of sulphur in piperidine are found to react with alkali sulphite in acid medium producing thiosulphate and a small quantity of trithionate. Similarly mono and dithiopiperidines react with sulphite in presence of acetic acid and give rise to tri and tetrathionates respectively. Perhaps this is the reason for the absence of thiopiperidine during acid hydrolysis of disulphur monoxide absorbed in solvents containing piperidine. The presence of piperidine in considerable concentration is known to react with higher polythionates (penta and hexa) producing thiosulphate and thiopiperidines.<sup>20</sup> The latter may react with excess of thiosulphate to give rise to tri and tetrathionate. Such reactions of thiopiperidines with sulphite and thiosulphate have been studied in detail and reported elsewhere.<sup>15</sup> Even a solution of thionyl piperidine behaves like a sulphite and hence it can react with mono and dithiopiperidines in acid medium giving rise to tri and tetrathionate.

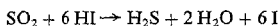
It has been shown by the present authors that piperidine thiosulphate can be prepared in solid condition by bubbling oxygen through a solution of sulphur in piperidine<sup>21</sup>. The unconsumed oxygen present in the products of combustion<sup>4</sup> might easily oxidise sulphur solutions in piperidine giving rise to piperidinum thiosulphate. Monothiopiperidine has been found to be one of the products of oxidation of sulphur solution in piperidine by oxygen in addition to the thiosulphate. Therefore it is reasonable to expect that thiosulphate may be obtained by all the above-mentioned reactions. But it is not practicable to estimate the amount of thiosulphate contributed from each of these reactions to the total quantity.

The fact that there is no elemental sulphur formed in alkali and acid hydrolysis reactions is further confirmed by the hydrogen iodide reaction. When the products of combustion of sulphur absorbed in carbon tetrachloride and toluene containing piperidine are reduced by hydrogen iodide, the entire quantity of sulphur is found to be converted into hydrogen sulphide.

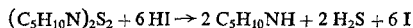
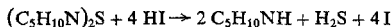
Disulphur monoxide solution in carbon tetrachloride has been observed to oxidise hydrogen iodide liberating iodine and hydrogen sulphide in the ratio of 3:1 according to the equation :



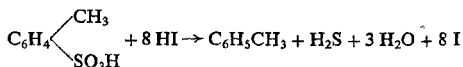
Similarly sulphur dioxide solutions have been shown to undergo reduction giving rise to iodine-hydrogen in the ratio of 6:1 as per equation :



In the present investigation, where piperidine is used to absorb the products of combustion, in an inert solvent, both the disulphur monoxide and sulphur dioxide are fixed by the piperidine. If the products of combustion contained only disulphur monoxide which was not bound by piperidine, the ratio of iodine to hydrogen sulphide in the hydrogen iodide reaction would be 3:1; if only sulphur dioxide were present, this ratio would be 6:1. When both disulphur oxide and sulphur dioxide are present, this ratio should be between 3:1 and 6:1. It has been shown by other reactions that the products of combustion absorbed in carbon tetrachloride and toluene containing piperidine include thiopiperidines also. Mono and dithiopiperidines have been found to react with hydrogen iodide according to the following equations:<sup>18</sup>



As per these reactions, presence of thiopiperidines should reduce the ratio of iodine to hydrogen sulphide. But the actual experimental values obtained with carbon tetrachloride and toluene solutions containing piperidine are 1:5.8 and 1:6.3 respectively. This departure from the expected results may be attributed to the presence of some oxygenated compound in the system. The amount of iodine liberated in this reaction will be considerably greater than that liberated when disulphur monoxide and thio-piperidines are treated with hydrogen iodide. One oxygenated compound that may be present in a small quantity is toluene sulphonic acid in toluene solutions as reported by Schenk<sup>22</sup>. This is expected to react with hydrogen iodide as per equation :



The quantity of toluene sulphonic acid could not be determined in the present investigation. But the above reaction shows that this compound if it is present even in small amounts can enhance the iodine to hydrogen sulphide ratio when it is reduced by hydrogen iodide.



It is impracticable to compute the amount of disulphur monoxide and sulphur dioxide present in the absorption medium when piperidine is used in the organic solvent to absorb the products of low pressure combustion of sulphur in oxygen. It has already been pointed out that hydrogen iodide reaction cannot be used for anisole solutions.

The products of alkali hydrolysis of disulphur monoxide solutions in carbon tetrachloride, toluene and anisole containing piperidine are more or less similar. The products of acid hydrolysis also resemble each other. These are sulphite, thiosulphate trithionate and tetrathionate.

In conclusion, it may be stated that when the products of combustion of sulphur in oxygen at low pressure are passed through cooled organic solvents, fairly pure solutions of disulphur monoxide can be obtained in carbon tetrachloride. Toluene and anisole solutions contain considerably large quantities of sulphur dioxide associated with disulphur monoxide. It is thus clear that for accurate studies with disulphur monoxide carbon tetrachloride solutions are preferable in order to avoid the contamination with sulphur dioxide. However, in the presence of piperidine, the solvent effect is nearly the same in all cases on account of the reactivity of piperidine with oxides of sulphur. The influence of piperidine is observed in the variation of the products of hydrolysis in alkali and acid media. This difference in behaviour could be understood by studying some systems involving piperidine compounds of sulphur.

#### ACKNOWLEDGMENT

The authors are grateful to Professor M. R. A. Rao for his interest in the work and for helpful suggestions.

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